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Raman and surface-enhanced Raman spectra of flavone and several hydroxyl derivatives. *Journal of Raman Spectroscopy* (in press).

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ON THE FIRE HISTORY OF GALICIA

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Introduction

The area of Campo Lameiro (NW Spain) harbours one of the largest concentrations of rock art in the northwest of the Iberian Peninsula. By means of the creation of a museum, it is designed to become a major tourist attraction. However, due to the lack of archaeological remains in the soils surrounding the petroglyphs, methods that are not conventional in archaeology were needed to unravel the anthropogenic history of the area. The chemical fingerprint of the organic matter is studied for this purpose.

While biomarker-evidence of ancient crop cultivation and stock-breeding systems was looked for, it seems likely that any such signal was disturbed by the intense fire regime of the area. There are several arguments for studying the fire history of the area in detail: (1) human-induced deforestation by use of fire had been hypothesised to start around 5500-6000 BP, (2) frequent occurrence of fire may indicate cultivation-regeneration cycles, and (3) if a significant amount of the organic matter had been thermally altered, this should have great consequences on the evolution of the soil because burning residues are known for their resistance against biodegradation, and thereby change the current theories on the genesis of the soil type involved (Atlantic ranker).

Unfortunately, the impact of fire on organic matter chemistry is still a source of controversy. A standardised method to quantify black carbon (BC), i.e. the common denominator of all burning residues (e.g. partially charred organic matter, charcoal and soot), does not exist. This is mainly a consequence of the differences between the various BC phases, but also of our lack of knowledge on how BC evolves from a chemical point of view that renders it very difficult to identify, let alone quantify, ancient BC or its derivatives. In this short communication the various lines of evidence pointing to a central role of fire events are summarised, followed by a discussion on the implications of this hypothesis.

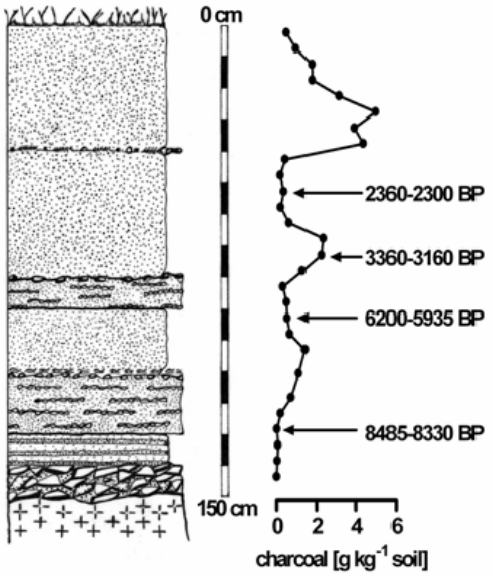

Figure 1. Macroscopic charcoal content and radiocarbon ages (2σ cal BP) of a soil profile from Campo Lameiro.

Abundance of large charcoals

The landscape of the study area has been formed in the course of thousands of years of erosion and sedimentation (colluviation) and therefore the depth profiles of the colluvial soils reflect a historical record. As the soils contain large charcoal particles (> 2 mm, obtained by wet sieving of soil) throughout the profiles, the concentration profile of such macroscopic charcoal fragments reveals evidence of burning episodes. Figure 1 shows an example of a soil with the macroscopic charcoal content curve, and some radiocarbon ages. It appears that charcoal is concentrated in three soil layers. Macroscopic charcoal is unequivocal evidence of fire, but its concentration is only small - between 0 and 6 g/ kg soil.

Micromorphology & SEM

Analysis of cut epoxy-impregnated soil blocks with scanning electron microscopy (SEM)

revealed unambiguous evidence of charred organic matter, i.e. homogenised cell walls (Figure 2A). Also, SEM micrographs indicated that the majority of the BC fragments had undergone strong fragmentation and degradation.

Analysis of thin sections (impregnated soil blocks cut to a ~20 µm film on glass) indicated that the soils are also loaded with smaller charcoals. Sometimes these were easily recognised, such as in Figures 2B and 2C, where the charcoal fragments occur isolated or in a brown-coloured organic matrix, respectively. Others, as shown in Figure 2D (a charcoal fragment in the top-left corner of the photo), cannot be easily distinguished from non-charred organic matter. The opaque and largely "amorphous" organic matter in that particular photo is commonly thought to be the product of *melanisation* (i.e. the process of dark colouring of organic bodies by accumulation of very dark to opaque organic plasma), but its resemblance to charcoal suggests that this very dark to opaque organic plasma may well be derived from BC.

Image analysis of 216 photos from four soils allowed us to infer that at least 10% of the organic matter derives from fire residues, but much more BC may be present in the twilight fractions of the organic matter as opaque organic plasma.

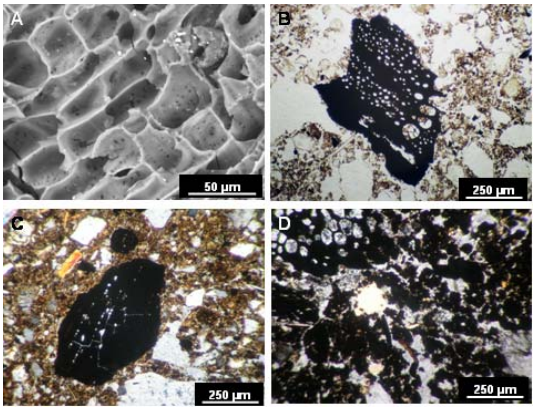

Figure 2. Various BC appearances. A: scanning electron microscope; B-D: petrographic microscope.

Organic matter chemistry

The lack of knowledge on the chemical composition of ancient BC severely limits our knowledge on the impact of charring on organic matter preservation over long time scales. Black carbon is oxidised and attacked by decomposer organisms after its formation, and with time it increasingly resembles the so-called "highly aromatic humic acids". Although increasing evidence seems to indicate that these "highly aromatic humic acids" are actually derived from BC, our current lack of unambiguous proof of this parity renders it virtually impossible to demonstrate whether ancient organic matter had undergone charring or not.

Characterisation of BC is traditionally achieved with solid state ^{13}C NMR (nuclear magnetic resonance). However, this method's structure resolving power is very limited as it can only determine chemical environments of individual C atoms, not the arrangement of these atoms. Pyrolysis-GC/MS allows for a more detailed characterisation of BC, but is not often performed for that purpose as the pyrolysis step that precedes GC/MS separation/identification invokes thermal alterations that may interfere with those invoked by natural fire.

Table 1. Summary of component class distribution obtained using pyrolysis-GC/MS. Average and standard deviation of 27 samples (bottom sample of the profile in Figure 1 omitted). PAH = polycyclic aromatic hydrocarbon. TIPA = total identified peak area.

	benzenes (% of TIPA)	benzonitrile & quinoline (% of TIPA)	PAHs (% of TIPA)	Total aromatics (% of TIPA)
Average	31.9	3.7	6.4	82.0
St. Dev.	4.1	0.9	1.7	4.8

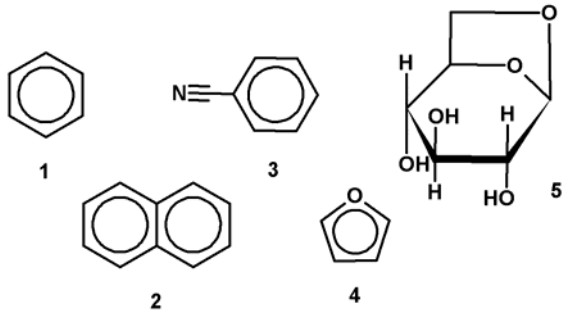

Table 1 summarises the results of pyrolysis-GC/MS of NaOH-extracted organic matter from the soil profile shown in Figure 1. The pyrolysate is dominated by benzenes (mainly benzene (compound 1) and toluene), polycyclic aromatic hydrocarbons (PAHs, e.g. naphthalene, compound 2), N-containing compounds (e.g. benzonitrile, compound 3), carbohydrates (predominantly furans, compound 4), lipids (straight-chain aliphatics) and (methoxy)phenols. Especially the large amounts of benzenes, benzonitrile and PAHs, and the sum of all aromatic pyrolysis products including heterocyclic aromatics (Table 1), are

widely accepted as evidence of thermal modifications. The pyrolysis step is almost certainly not responsible for these modifications, as pyrolysis-GC/MS of a myriad of different non-charred biomolecules does not yield large amounts of these compounds.

The very low contribution of levoglucosan (compound 5) and other levosugars, which are the major pyrolysis products of intact polysaccharides, indicates that the carbohydrate component is highly degraded. Indeed, Pastorova *et al*. (1994) showed that heating of cellulose prior to pyrolysis-GC/MS causes a loss of levoglucosan and a relative increase in the contribution of furans, and PAHs at higher temperatures. The PAHs are inversely related (r^2 = 0.74, $P < 0.001$) to the sum of all carbohydrate markers (Figure 3), which may suggest that the PAHs originate from carbohydrate material that was modified during fire evens. If this interpretation is correct, the decrease in PAHs and increase in carbohydrate markers around 6000 BP (ca. 90 cm, see Figures 1 and 3) indicates a drop in burning temperature around that time. A dramatic increase of human impact on the landscape is known to initiate around 6000 BP, so this potential change in burning temperature may represent a change in the nature of the fire from natural forest fire to human-controlled burning of less-developed vegetation communities, which may reasonably be expected to have taken place at lower temperatures.

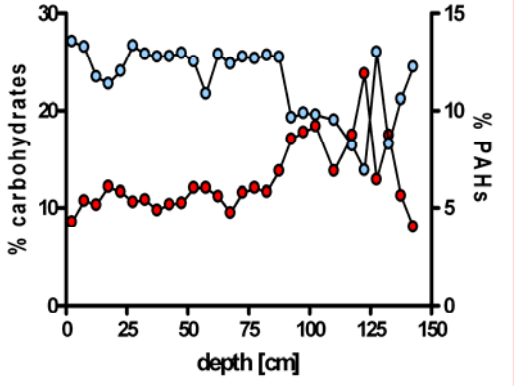

Figure 3. Carbohydrates (in blue) and polycyclic aromatic hydrocarbons (PAHs, in red) as determined by pyrolysis-GC/MS.

In summary, pyrolysis-GC/MS yields circumstantial evidence of burning (highly aromatic organic matter and the presence of fire markers such as PAHs). Whether the PAHs-to-carbohydrate ratio indeed reflects a change in burning circumstances has yet to be elucidated.

Ramifications

Archaeology

The abundance of charcoals and highly aromatic organic matter in all samples strongly suggests that fire has been very important in the area for at least 8000 years. The deforestation of NW Iberia around 5500-6000 BP coincides with a drastic change in the PAHs-to-carbohydrate ratio. We speculate that this event marks the change from the incidence of natural forest fires to controlled burning afterwards. If this is correct, the area could well have been used by ancient societies as early as 6000 BP. The large charcoal fragments could then derive from carbonized heather stands that were allowed to recover periodically to allow the soil to recover.

Black Carbon composition

The high resolution sampling approach provided important knowledge on the composition of ancient organic burning residues. PAHs may be the product of incomplete carbohydrate combustion at high temperatures. Highly aromatic humic substances again showed circumstantial evidence of thermal modifications. Benzonitrile is suggested as a potential BC marker when analysed by pyrolysis-GC/MS. This information brings us closer to understanding the contribution of BC to resistant organic matter, and the recognition of this material by pyrolysis-GC/MS.

Soil genesis

Present theories of the evolution of the dominant acidic soils of the studied area focus on stabilisation of organic matter by "active Al" released upon weathering of the parent rock, (i.e. migmatitic granite). Charring is now put forward as a complementary reason for the organic matter's resistance to microbial decay. The formation of resistant organic matter through fire, in combination with sorptive preservation of Al-organic matter complexes, may well explain how large amounts of organic matter have accumulated in a humid temperate climate such as that of Galicia.

Acknowledgements

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